Time Resolved Measurement of Ecosystem-Atmosphere NH3 Exchange Using the Eddy Covariance Technique

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Outline

- **Motivation –Mechanistic Studies Benefit from Time Resolution**
- **Instrument Description – Laser Spectrometer & Fast Sampling System**
- **Initial Results - Field Tests at Richmond, CA**
- **Conclusions**

Unit Conversions

- Units for NH_3 flux are chosen to match measurement time scale ($\mu mol\ m^{-2}\ hr^{-1}$)
- Conversion to other units

1 kg N/ha/yr = 0.82 or ~ 1 $\mu mol\ m^{-2}\ hr^{-1}$

1 ng N/m^2/s = 0.26 or ~ ¼ $\mu mol\ m^{-2}\ hr^{-1}$

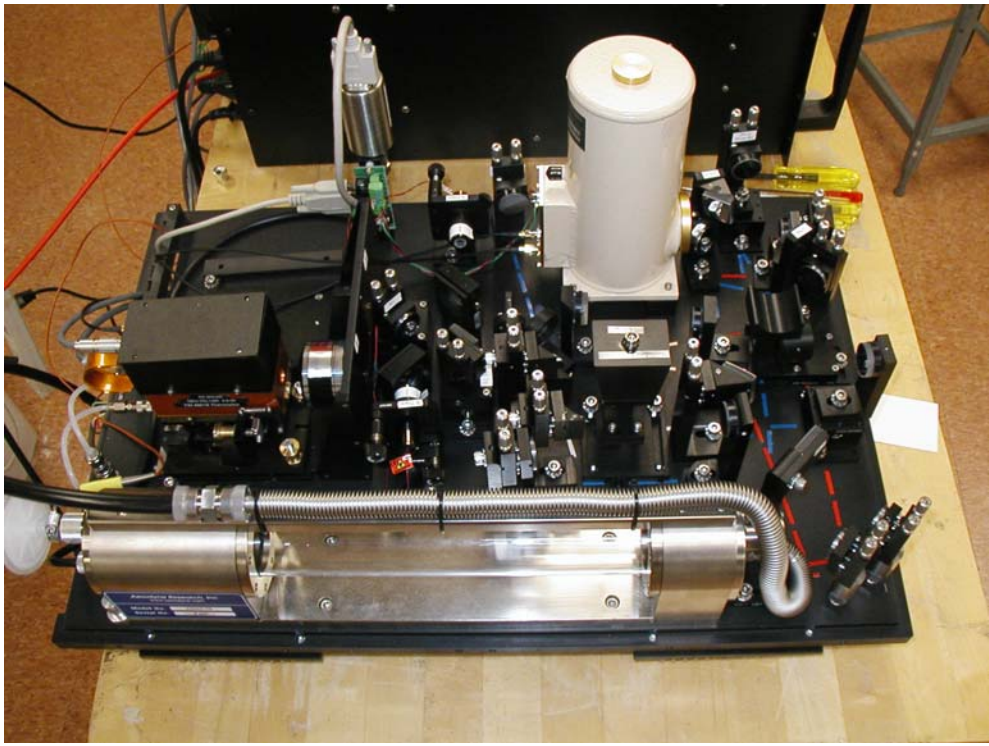
Comparison of Some NH_3 Fluxes

Ecosystem Description	NH3 Flux μmol m^{-2} hr^{-1}		Reference
Deposition	min	max	
Forests, Lake Tahoe	1.0	4	Tarnay, 2001
Grasslands, SF Area Roads	2.4	12	Weiss, 1999
Modeled Dry Dep. To CA	0.6	24	Weiss, 2005
Modeled Dry Dep to UK	0.1	12	Fornier et.al., 2005
Grass near S.Carolina Farm	78	544	Phillips et.al., 2004
Emission			
Riparian, (Un)grazed	1	58	Walker et.al., 2002
Agricultural Field	78	3500	Zhu et.al, 2000
Agricultural Field	2160	10802	Meyers et.al., 2003

Technical Approach (1)

Sensitive NH_3 analyzer

- **11 μm Quantum Casade Laser Spectrometer**
- **Low-volume multi-pass absorption cell**
- **Separate channels for frequency lock and gain normalization**
- **Sensitivity: 300 pptv RMS @ 10 Hz sample rate**
- **Stability: 40 pptv RMS over 100 s integrations**



11 μm NH_3 Spectrometer
Aerodyne Res. Inc

Technical Approach (2)

Fast-response Gas Sampling

1) High sample flow

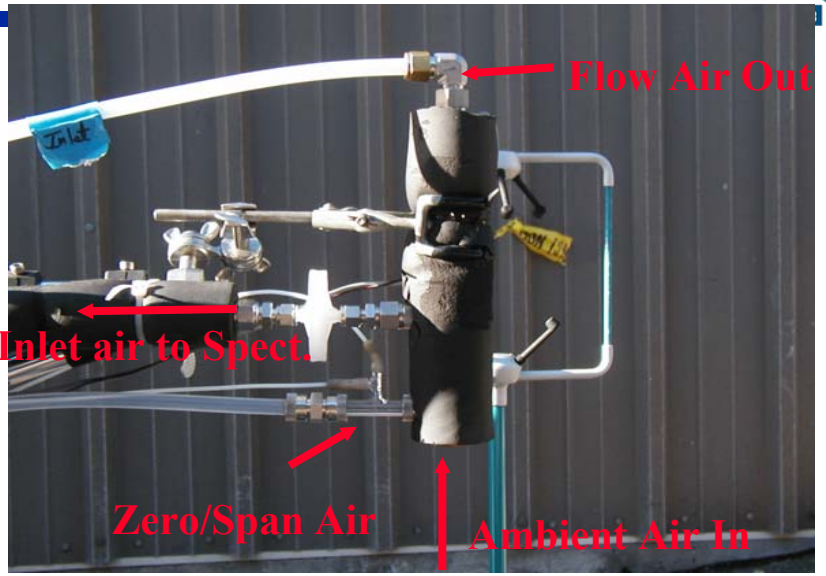
- — ~ 20 liters min^{-1} @ 1 atm
- — > τcell ~ 0.15 s

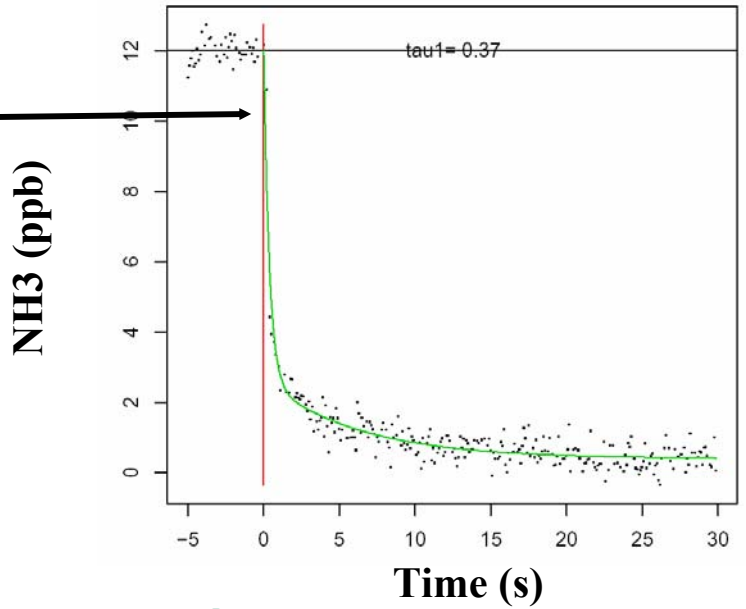
2) Heated Inlet Manifold

- — Materials:
  - PFA Teflon
  - Siloxyl coated glass
  - T > 35-40 C all lines

3) Automated Test of Transient Response

- — Zero/span test every ½ hr
- — Fit double exponential response
  - 80% response $\tau 1$ = 0.3-0.4 s
  - 20% response $\tau 2$ = 4 s
- — Measured response used to correct NH3 flux for loss of signal due to smoothing
  - Typically factor 30-50%





Technical Approach (3)

Field package for extended outdoor operation:

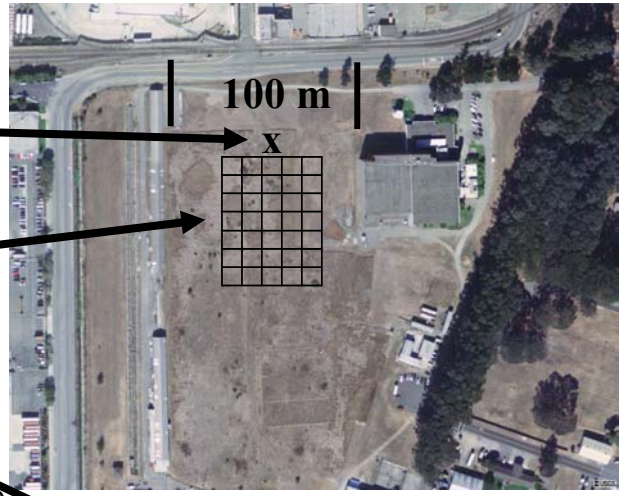
- **Automated calibration**
- **Automated LN2 fill**
- **Automated data transfer**
- **Size 2m x 1m x 1m**
- **Weight 220kg**
- **Power 25 Amps @ 120VAC**

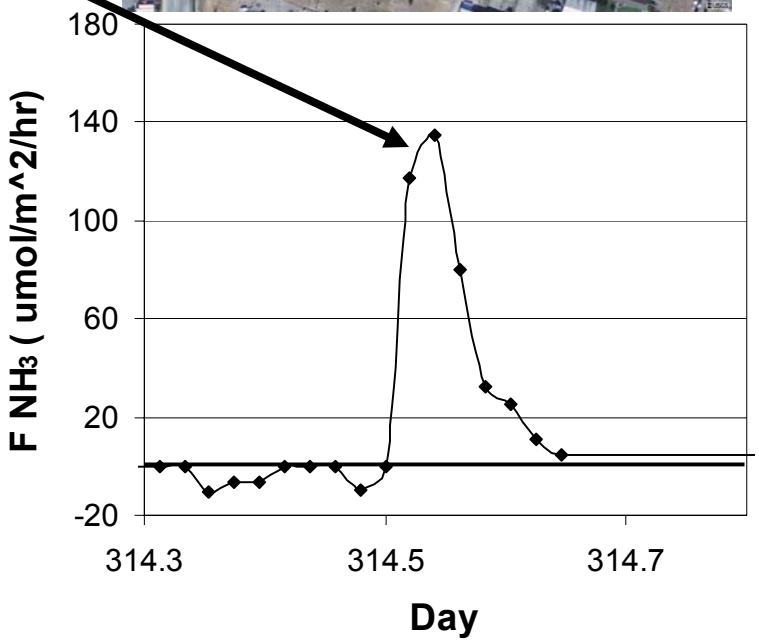
Instrument Package on Scaffold, Richmond, CA

NH_3 Detector
NH_3 Inlet
CO_2/H_20 Sensor
Sonic anemometer

Field Testing (1): NH_3 Release Experiment

- Field test at Richmond, CA
- Instrument located on N. side of shrub/grass field
- Fill array of cups on 10m grid containing 4% NH_4OH solution
- Large initial NH_3 flux observed
- NH3 flux decayed exponentially w/ time as NH_4 depleted
  - Integrated flux equals 25% of NH_4 initially applied to cups
- Estimation of flux footprint, advection, and deposition to canopy in progress

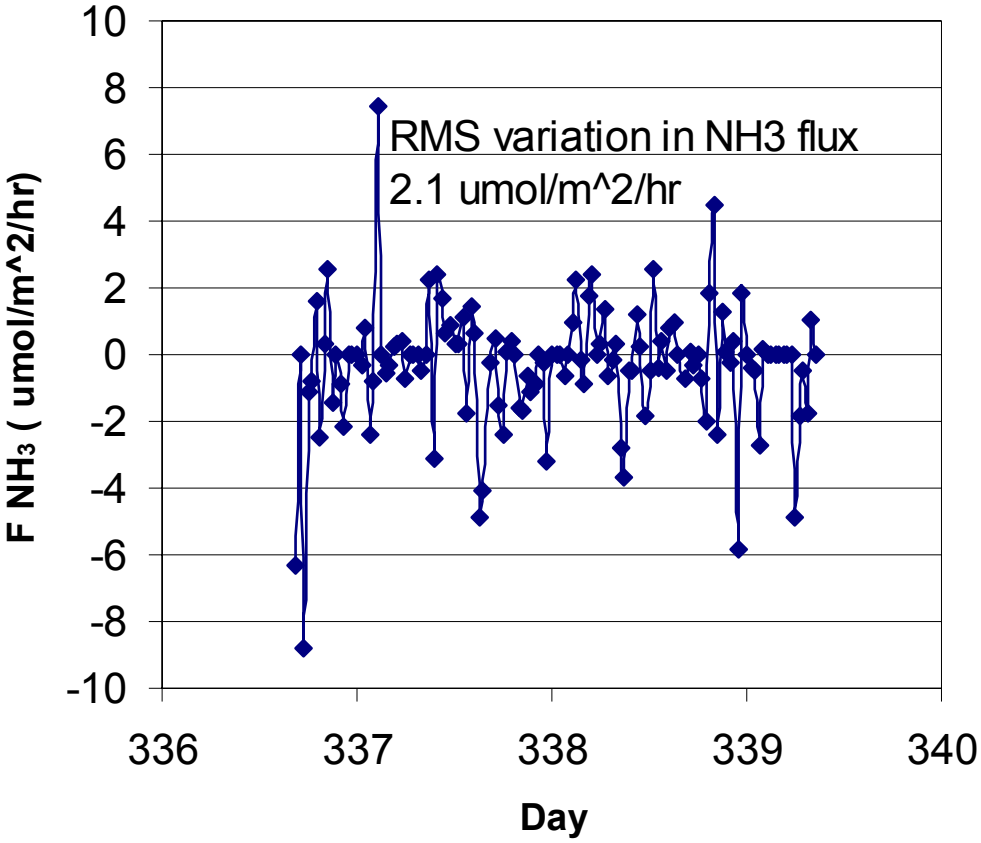




Field Testing(2): Sensitivity Test

3 Day test

- **Richmond, CA**
- **No NH_3 released**
- **Small variations in flux**
  - **RMS = 2 μmol m^{-2} hr^{-1}**
- **Sensitivity sufficient for measurement campaigns in many natural ecosystems**
- **Ongoing development will likely improve sensitivity further**



Conclusions

- Time resolved NH_3 flux measurements valuable for quantification of diurnal-seasonal variations in NH_3 deposition and emission
- Sensitive eddy covariance measurements of NH_3 flux have been achieved
  - —Instrument sensitivity sufficient for measurement in variety of settings
- Identification of future field sites in progress

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